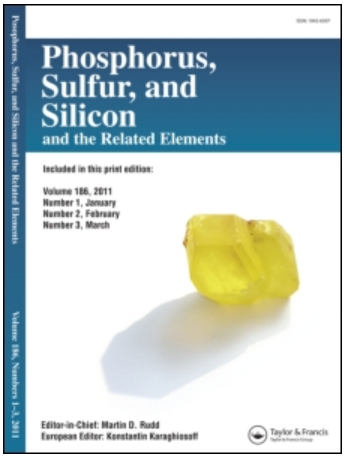

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Direct Synthesis of New Types of Phosphazene Polymers using Alkaline Carbonates

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The use of potassium or cesium carbonates as proton abstractors to substitute chlorine by aryloxy groups in chlorophosphazenes is a convenient synthetic method that has led to the discovery of new types of phosphazene high molecular weight polymers, including quiral binaphtoxy polyphosphazenes.

Keywords: Polyphosphazenes; biphenoxy; binaphtoxy; quiral polymers

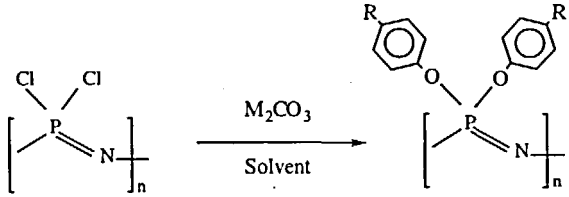
INTRODUCTION

Polyphosphazenes are a very important class of inorganic polymers [1], consisting of $-(R_2)P=N-$ repeating units. Cyclic and polymeric aryloxy-phosphazenes can be prepared by reacting $[N_3P_3Cl_6]$ or $[NPCl_2]_n$ with the appropriate phenoxides[2], but many other alternatives has been proposed to improve the synthetic procedure [3], [4]. We present here a brief summary of the applications of the systematic use of alkaline carbonates, K_2CO_3 and Cs_2CO_3, as bases in the direct reaction between chlorophosphazenes and phenols. In fact, it is not only a very convenient synthetic method, but it has also enabled us to prepare the first polyphosphazenes containing cyclic biphenoxide repeating units $[N=P(O^{-R}-O)]$ (polyspirophosphazenes). This new type of linear polymers can be extended to include the optically active polyphosphazenes with quiral binaptoxy groups.

THE USE OF ALKALINE CARBONATES

A few years ago we reported that trimeric $[N_3P_3(OC_6H_4\text{-}R)_6]$ or polymeric aryloxyphosphazenes $[NP(OC_6H_4\text{-}R)_2]_n$ can be prepared very conveniently by the direct reaction of the corresponding chlorophosphazenes $[NPCl_2]_n$ and the phenols $HO\text{-}C_6H_4\text{-}R$ in the presence of K_2CO_3, using acetone for the cycles, and THF for the polymers [4]. The workup was very simple, and the yields were high. However, it had an important limitation; in the case of the less acidic phenols (R = H or an electron releasing group such as Bu^t or OCH_3) the chlorine substitution in the high molecular weight polymers were too slow to be convenient.

Later, we found that the use of Cs_2CO_3 in place of K_2CO_3 is much more efficient making the method also suitable for the non-activated phenols as well as for the aliphatic alcohol $HOCH_2CF_3$, for the preparation of the cyclic phosphazenes and the high molecular weight polymers [5] (Scheme 1).



M : K or Cs.
Solvent : Acetone for cycles;
THF for polymers

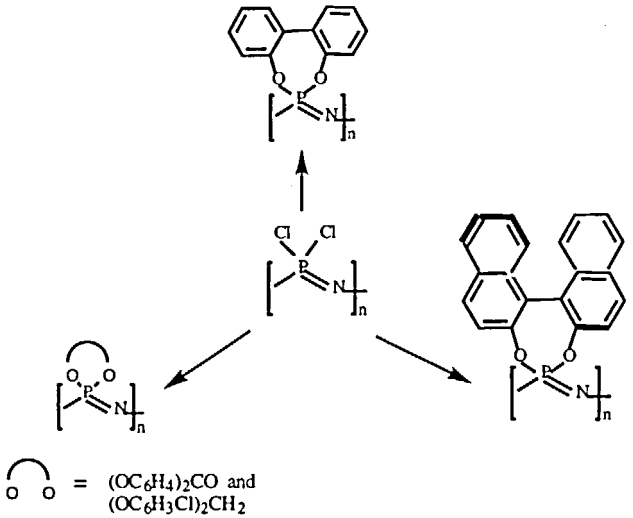
Scheme 1

POLY(SPIROPHOSPHAZENES) AND QUIRAL POLYMERS.

While extending the use of this technique, we discovered[6] that the reaction of $[NPCl_2]_n$ with the biphenol 2,2'-dioxybiphenyl $(HO\text{-}C_6H_4\text{-}C_6H_4\text{-}OH)$ and K_2CO_3 in THF leads to the synthesis of the very soluble linear polymer $[NP(O_2C_{12}H_8)]_n$ having Mw of the order of 500.000. The analytical and spectroscopical data evidenced the formation of a "spiro ring" in each phosphorus. The synthesis of those uncrosslinked materials were rather surprising, because of the bifunctional nature of the biphenol.

However, the products of those reactions contained variable amounts of poly-tetrahydrofuran (PTHF), responding to the formulae $[NP(O_2C_{12}H_8)\cdot x(OC_4H_8)]_n$. This showed that the $[NPCl_2]_n$ as prepared by the method described by Magill et al.[7] can polymerize the THF, and that the resulting PTHF is not separable from the $[NP(O_2C_{12}H_8)]_n$ polymers. The PTHF could be avoided using 1,4-dioxane as solvent [8].

Similarly to the 2,2´-dioxybiphenyl, other biphenols like bis (2-hydroxyphenyl)ketone, $[(HOC_6H_4)_2CO]$; bis(2-hydroxy-5-chlorophenyl)-methane, $[(HOC_6H_3Cl)_2CH_2]$, reacted directly with the $[NPCl_2]_n$ to give soluble uncrosslinked polymers[9]. (Scheme 2)

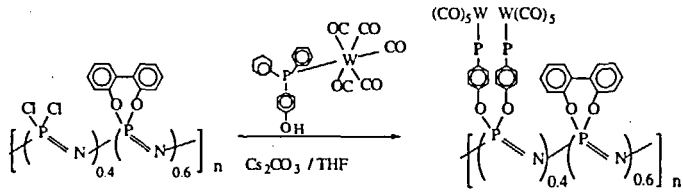


Scheme 2

Those results led us to use the binaphtols to prepare the quiral polyphosphazenes of general formulae (+) and (-)$[NP(O_2C_{20}H_{12})]_n$, although in moderate yield[9]. (Scheme 2). Those polymers are only sparingly soluble, but later we found that its solubility can be greatly enhanced by heating moderately near 120°C. This treatment reduces the Mw from the initial 10^6 to ca 300.000. This observation had an interesting synthetic application, because the polymers could be prepared in higher yields than previously published, by including a heating step in the procedure.

OTHER APPLICATIONS

Finally, we have observed that the mild reaction conditions required by the use of cesium carbonate allows the direct replacement of a chlorine atom by a *p*-hydroxophenyldiphenylphosphine complex in a chlorophosphazene co-polymer[10]. (Scheme 3). This means a considerable simplification over the previous known multistep method[11].



Scheme 3

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